# SYNOPSIS OF THE Ph.D THESIS

## Effect of Organic Dopants on Structural, Optical, Electrical and Thermal Properties of Polymer Composites

Insulating and intrinsically conductive polymer (ICP) blends designed with synergetic approach play a vital role in device fabrication and industrial growth of the country. Invention of an efficient, durable and cost-effective plastic electronic devices will be the best alternatives for the conventional solid state electronic devices. In this regard, the investigations on ICPs and their composites with insulating matrix are to be applauded in the field of research. The backbone of ICPs is a uniform sequence of σ–bonds, which provides the necessary stability against the external perturbation like electric field or electromagnetic field and the alternating π–bonds participate in conducting process, actively leaving intact the backbone of σ–bonds. Broad emission spectra with the possibility of multi-wavelength emissions, strong absorption coefficients, high fluorescence quantum efficiencies with large Stokes shift and good charge transport properties are the extra credits of these ICPs needed for the construction of optoelectronic devices such as transistors, photodiodes, organic photovoltaic (OPV) devices, organic light-emitting diodes (OLEDs) and efficient display devices. The drawback of ICPs is their poor solubility in common solvents due to their rigid backbone structure. This problem is solved by blending or doping ICPs with insulating polymers which remove the brittleness and lack of processibility. This not only increases the film forming ability of ICPs but also influences their spectroscopic and physical properties such that a new material with desired mechanical and functional properties can be obtained [1]. Another drawback of the semiconducting polymers is they are expensive (exorbitant pricing). Reducing their cost is the prerequisite for their commercialization which can be achieved by blending or doping of ICPs with the usually available cheap insulating polymers[2-4]. Besides the economic reasons, properties of electroluminescent polymers and characteristics of their interfaces with the inert polymers play vital research importance and applications. Even the photovoltaic devices, in which conductive–insulating blends are used as the active material, have proved to give an excellent performance than those devices merely using conducting polymer as the

active material. The phase separation behaviour of conducting–insulating blends can yield bulk heterojunctions that can cause efficient excitation-dissociation needed for a photovoltaic cell [5-7].

Among light emitting polymers (LEPs), the most frequently used polymers in optoelectronic devices are the Poly p-phenylene vinylenes (PPVs) and their derivatives, Poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and Poly [2-methoxy, 5-(2-ethyl-hexyloxy)-p-phenylene-vinylene] (MEH-PPV). Poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] is a di-alkoxy substituted poly(p-phenylenevinylene) polymer with HOMO and LUMO orbital positions at 5.4eV and 3.4eV respectively and a band gap of about 2.2eV [8-11]. MEH-PPV is the PPV derivative with methoxy and 2-ethylhexiloxy substituents on phenyl rings, with HOMO =5.3eV & LUMO= 3.0eV and an energy gap of 2.3eV. Their thin films can be effectively used in energy harvesting and displaying devices like solar cells, LEDs and far-infrared laser amplifiers, photo-detectors and high-speed electro-optical modulators [12-18]. Among the insulating polymers, PMMA has a drastic role in organic electronics because of its low cost, good tensile strength, high transparency, low glass transition temperature, enough thermal stability and can be used as a glass substitute on a wide range. PMMA absorbs only a trace amount of light and UV radiation so that the small amount of absorbed radiation cannot breakdown the molecular bonds within the material and makes it well suited for long term weather resistance. The unique properties of PMMA make it the most commercially important acrylic available till date [19-20].

Lot of reports can be quoted regarding the investigations on MDMO-PPV, MEH-PPV and their composites with the other conjugated as well as the insulating polymers. M. P. Joshi et al. studied the charge transport properties in thin films of MDMO- PPV cast from chloroform, toluene and chlorobenzene and reported the maximum hole mobility in chlorobenzene. The inter-chain interaction was highest in chlorobenzene and was lowest in chloroform [21]. Li-Ting Lee at al. reported the phase-separated structures in MDMO-PPV/PMMA by scanning near-field optical microscopy (SNOM). They noticed, the PMMA-rich phase with less fluorescent emission and MDMO-PPV-rich phase with highly fluorescent emission regions, purely determined by the solvent quality. They concluded with the necessity of hydrophilic substrate for maintaining the continuous structures for PMMA [22].

Dorota Jarzab et al. carried out the combined photoluminescence and morphological investigations on MDMO-PPV/PBFF blends and proved the partial Forster energy transfer from PBFF to MDMO-PPV. The phase segregation was observed for MDMO-PPV concentrations higher than 10% on the host PBFF and photoluminescence signals of varying intensities and shapes were observed on the whole surface [23]. Takatsugu Wakahara et al. marked that the photoluminescence originating from the conjugated MDMO-PPV polymers was effectively quenched in the composite films of MDMO-PPV and P3HT on doping with $C_{60}$ nano-whiskers, indicating a strong interaction between the conjugated polymer and $C_{60}$NWs[24]. Offermans et al. studied the photo-physical properties of a solution processed blend of MDMO-PPV and PCNEPV. The photoexcitation of the either of the polymers results in the formation of a luminescent exciplex at the interface of the two materials. The exciplex can decay to the lowest triplet state of MDMO-PPV, resulting in the field-enhanced quantum yield [25].

Chien-You Su, at el. studied the optical behaviour of MEH-PPV/PMMA with revelation of the individual effects of MEH-P16PV concentration, PMMA molecular weight, the blending ratio and concluded that ultimately it is the interaction between MEH-PPV and PMMA in solution to determine the optical performance of solution-cast thin film [26]. Antonio C. C. Ribeiro et al. examined the photoluminescence in MEH-PPV/PMMA blend films and reported unexpected photo-luminescent behaviour in solutions and films, related to different excitons modulated by MEH-PPV conformations, unravelling the singlet and triplet state energies detected through time-resolved fluorescent spectroscopy [27]. Adachi Takuji et al. examined the fluorescence polarization anisotropy of single polymer chains of MEH-PPV isolated in PMMA matrix, evidencing its rod-shaped conformations [28]. Shen-Yi Hsu et al. observed the blue shift of PL spectrum in MEH-PPV/PMMA blend when the weight ratio is smaller. The new PL spectrum indicated that the excitons in MEH-PPV chains are interrupted by the PMMA and thus emitting light as PPV oligomers [29]. LEDs made of polymer blends are proved to be efficient than those prepared from neat ICPs because of the easily achieved color tuning, emission line narrowing and voltage-tuning in such devices. A. D. Scaccabarozzi et al. constructed organic field-effect transistors (OFETs) and organic

solar cells (OPVs) with semiconductor/insulator blends without detrimental effects on the resulting device characteristics even at high contents of the insulator [30,31].

The TCNQ molecule (7, 7, 8, 8-tetracyanoquinodimethane) and its radical ion have drawn the attention of researchers in recent years in the field of organic electronics. TCNQ is very strong electron-acceptor organic molecule, with electron affinity between 2.88eV and 3.38 eV. With this property it is able to form a large number of charge transfer complexes with metallic or organic donors. Some of the TCNQ complexes are superconductive at comparatively high temperatures. It is useful in preparing molecule-based organic magnets and also as enzyme-based biosensors. Metal-free TCNQ and its derivatives are used as monomeric organic cathode materials for lithium-ion batteries, that can produce high cell voltage [32-34]. Its salt exhibits one-dimensionally stacked polymeric crystalline structure with metallic electric conductivity. These properties of TCNQ are influential in organic electronics preferably in the construction of transparent electrodes, photovoltaic cells, light-emitting diodes, dielectric films, Schottkey diodes, FETs etc. The partial Paramagnetism and electrical conductivity are the focusing properties for researchers regarding TCNQ.

Harvesting the abundant solar energy to win over the energy crisis is another aspect of present-day research. The first-generation silicon-based cells and the second-generation thin film solar cells are not affordable to common people. On the way to search for a cost-effective cell, plastic solar cells are found to be promising but low efficiency is the main drawback. Achieving higher efficiency photoactive materials or solar cell is a global challenge for researchers [35-36]. The Bulk Hetero Junction (BHJ) concept of the donor-acceptor system (PN junction) has provided remarkable progress in the efficiency enhancement due to formation of multi-P-N junctions, by which exciton diffusion mechanism and the charge collection rate have been significantly increased. Among acceptors, modified fullerene [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) has opened a new path of research because of its good transport property and stability. Optimization of bulk junction blends of P type polymers MDMO-PPV, MEH-PPV and Poly[3-hexylthiophene-2,5-dily) (P3HT) with PCBM as the N type acceptor are studied and reported in the last section of this thesis.

## Characterization Techniques Used:

Polymer composite films are characterised with different experimental techniques including UV-Visible, fluorescence spectroscopy, Impedance Analyzer, FTIR, XRD, SEM, TEM, EDAX, AFM, etc. UV-Visible absorption spectroscopy is used for investigation of optically induced electronic transitions and aids to find the band structure as well as energy gap in crystalline and non-crystalline materials. In the present work UV-Vis investigations on the samples are done with Shimadzu UV-1800 Spectrophotometer and Jasco UV-Vis NIR V 670 spectrometer of USIC, Fluorescence investigations are done using Fluoromax Plus CP Spectrofluorometer, 0124D-1816-AFMPLUS,HORIBA. AC conductivity is also helpful in understanding the chemical and physical structures of polymer composites [37]. Agilent 4294A Precision Impedance Analyzer is used to determine AC conductivity. The Current –Voltage (I-V) study of composite films can be carried out using two probe or four technique. The conductivity is calculated by measuring resistance for the known area and thickness of the polymer film and using the relation $\sigma_{dc}$ =d/RA (S/M).DC conductivity measurements are carried out using Keithley 236 Source Measure Units with Trigger Controller.

Fourier Transform Infrared spectroscopy (FTIR) is an extensively used method for the investigation of polymeric systems. It gives the structural information such as molecular geometry, chemical bonds and also molecular interactions.IR Prestige-21Shimadzu FTIR Spectro-photometer is used in the present work for FTIR characterization.

Thermal stability of polymer composites is a key parameter in considering its application. The thermal properties of polymer composite materials can be studied as a function of temperature. Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) are the different techniques used in thermal investigations [38,39]. The samples here are characterized by TGA using TA-SDT Q600 TGA Unit using which the nature of degradation, degradation temperatures, stability of the samples are interpreted.

Polymers are not available in 100% crystalline state, they are available in amorphous state or as a mixture of both amorphous and crystalline state, i.e. a kind of semi crystalline state. Sharp bands in the X-ray diffraction pattern correspond to

crystalline orderly regions and defused bands correspond to amorphous regions. Information regarding crystallinity and crystal structure, crystal size of the material is available with XRD [40,41]. We have used Rigaku Miniflex 600 X-ray diffractometer for XRD analysis.

SEM is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. By collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is obtained. SEM can achieve resolution more than 1 nanometre. Energy-dispersive X-ray spectroscopy (EDS) is a supplementary tool of SEM to determine the elemental analysis along with their composition in the SEM imaged sample. It is based on the principle that the electron beam hitting the sample will generate X-rays of varying energies determined by the elements from which it is emitted. A careful investigation of the energies of the emitted X-ray will reveal the elemental analysis along with the percentage composition. EVO MA18 with Oxford EDS is the instrument used in this work.

The AFM enables to get the three-dimensional surface profile unlike SEM which provides two- and three-dimensional projection. The reaction of the probe to the forces that the sample imposes on it is used to form an image of the three-dimensional shape (topography) of a sample. In addition to topographical images, other properties like stiffness or adhesion strength, electrical properties such as conductivity or surface potential, can also be measured.

## Specific Aims and objectives:

With lot of literature supporting the role of MDMO-PPV, MEH-PPV and their blends with PMMA in device fabrication, we planned to prepare the free-standing films of MDMO-PPV and MEH-PPV doped PMMA films in easy and economical way to get more insight into its optical, electrical, thermal, and structural behavior, to expand its horizon in the field of plastic electronics. Main intention of this work is to achieve the fluorescence tuning by impregnating it at very low doping concentrations in PMMA matrix, with the possibility of collapsed conformations in dilute solid. Wide competitive interest always exists to fabricate a good conducting

material with PMMA as the main matrix, to meet the demands of a conducting sample with the balanced synergetic like high electrical conductivity, good mechanical behavior enriched by thermal stability and durability. Our study reports the photo physics of the slightly doped MDMO-PPV/PMMA and MEH-PPV/PMMA samples as the core of investigations along with the electrical, thermal, and structural outcomes. Conducting -Insulating blends of Light emitting Polymers MDMO-PPV doped PMMA and MEH-PPV doped PMMA free standing films are prepared from solution cast method, maintaining very low doping concentrations. The samples in the experiment are excited with 340nm and 450nm separately for investigating their fluorescent response. Effect of the inert matrix PMMA on the chain aggregation behavior of MDMO-PPV and MEH-PPV are enunciated through the absorption-emission spectra. Photo physics parameters like absorption and emission shifts, Stokes shift, energy gap, Urbach energy are calculated. Thermal kinetics and evaluation of activation energy are done by Broido's, Horowitz - Metzger and Van Kravelin's methods and correlated. DSC, TGA XRD, FTIR, DC and AC conductivities are also investigated and interpreted. A relative interpretation on the chain aggregation behavior of MDMO-PPV and MEH-PPV by the common PMMA matrix is highlighted.

Since the TCNQ molecule (7, 7, 8, 8-tetracyanoquinodimethane) and its radical ion have drawn the attention of researchers in recent years because of its efficient charge transport nature and photoelectric properties, TCNQ/PMMA free standing films are prepared by the solution cast method. UV-Visible, Fluorescence, FTIR and other spectroscopic investigations are carried out. The changes in light absorption and emission properties, Stokes shift, band gap evaluation reported. Shift in the wave number, variation in intensity, interaction of dopant with host are identified with FTIR technique. Thermal techniques such as DSC, TGA, DTA and the analysis of the data obtained from these techniques like glass transition temperature ($T_g$ ), melting temperature ($T_m$ ), degradation temperature ($T_d$ ), heat of fusion $\Delta H$, weight loss derivative weight loss are reported. Using the XRD data, the crystallinity, interplanar spacing, crystallite size, of the samples will be analysed. Current – Voltage (I-V) characteristics techniques, and dc conductivity measurements are done using Keithley 236 Source Measure unit.

As another part of our research work, we prepared different Bulk Hetero PN Junction photo active blends using PCBM, P3HT, MEH-PPV and MDMO-PPV. Optimization of the P:N weight ratios in each system are done through UV-Vis spectroscopy. Band gap calculations are made using Tauc's plot. Optical constants like extinction coefficient and refractive index are calculated and interpreted through mathematical inversion method. Structural analysis by XRD, morphological studies by SEM, sample composition or purity by EDAX and the surface smoothness of the active film by AFM studies are carried out specially on MDMO-PPV:PCBM and reported. The results of these studies are presented in the following seven chapters.

## Chapter 1. Introduction

It presents basic information about the conjugated polymers, polymer composites, nanoparticles, and their effect on polymers with literature background. Light Emitting Polymers (LEPs), the need for LEP doped polymer films, the possible applications in plastic electronics are briefed. A chronological development in solar cells, necessity of Bulk Hetero Junction (BHJs) blends are also considered. The motivations for the current work, aim and objectives are enunciated.

## Chapter 2. Experimental Methods and Characterization Techniques

The second chapter gives various methods of preparation of polymer composites. A comprehensive description of different characterizations and measurement techniques along with their principles are presented. Spectroscopic investigations like UV-Visible spectroscopy and fluorescence, the structure related techniques such as FTIR, XRD, morphological related investigations like AFM, SEM, thermal analysis by DSC, TGA, DTA, electrical conductivity and dielectric investigation methods have been discussed in detail.

## Chapter 3. Switching the Photo Physics of MDMO-PPV Under PMMA Environment

This chapter describes the photo physics of the free standing films of MDMO-PPV doped PMMA films maintaining the minimum doping concentrations. MDMO-PPV film cast from chlorobenzene exhibits the absorption maxima at

337.3nm in the near ultraviolet and 496.6nm in the visible region. For 0.05% doped MDMO-PPV/PMMA films, altered absorption peaks have been observed at 340nm, 477.1nm and 559.3nm. With the increase in MDMO-PPV content, the peak at 477.1nm gets suppressed whereas the absorption peak corresponding to 559.3 nm is pronounced. The peak corresponding to 477.1nm (first peak) gets blue shifted while that corresponding to 559.3nm (second peak) gets red shifted relative to the absorption maximum of pure MDMO-PPV film (496.6nm) and the shifts are symmetric. The conjugation length of the dopant will be reduced, collapsing into extended or oligomer conformation of the conjugated chain. The simultaneous occurrence of the dual peaks is the indication of the presence of both extended and aggregated conformations of the dopant. The samples in the experiment are excited with 340nm and 450nm separately for investigating their fluorescent response. In the case of the doped samples, the emission spectra contains twin peaks centred at 530nm and 600nm caused by the two vibrational transitions 0-0 and 0-1 bands. At smaller doping concentrations, the emission at 530nm is dominant than that at 600nm, whereas with the increase in doping level, peak at 530nm gets suppressed followed by enhanced emission at 600nm and finally left with emission only at 600nm without the sign of that at 530nm. There exists symmetric correlation with respect to the emission of wavelengths as well as the intensity of the two peaks. The thermal degradation of PMMA occurs in three stages, characterized by the presence of three maxima in the DTG curve at about 127$^{o}$C, 328.4 $^{o}$Cand 380$^{o}$C. The dopant MDMO-PPV has very small glass transition temperature of about 45°C with negative influence on the $T_g$ of the host and reduces its glass transition temperature. But at the same time the phenylene units in MDMO-PPV being more rigid, its incorporation in PMMA has increased the stability of the doped samples. Activation energy is evaluated by Broido's method, Horowitz - Metzger method and Van Kravelin's method. The increase in activation energy with doping level of MDMO-PPV confirms the increased thermal stability of the samples as affirmed by TGA and DTG and DSC analysis. X-ray diffraction studies affirmed the semi-crystalline nature of PMMA. Pure PMMA has broad peak with Bragg's angle at $2\theta = 14.84^{o}$ and $29.1^{o}$. Absence of any prominent peak with the predominant broad peak indicates the partially crystalline and partially amorphous nature of PMMA. The dopant MDMO-PPV has reduced the crystallinity of the host, indicating that

inclusion of LEP in host matrix has disrupted the ordered polymer chain of the host. Since the doping level is minutely varied, the relative reduction or changes in the crystallinity is not noticeable. An increase in DC conductance with increase in the doping concentration has been noticed. The increased conductivity may be attributed to more charge carriers i.e., the delocalized π-electrons imparted by the doped MDMO-PPV into the PMMA matrix. The increase in dielectric constant at low frequency is assisted by the interfacial space-charge polarization. After certain frequency, the space charge carriers cannot line up with the field and the alternation of their direction lags behind the field, which results in the reduction of the dielectric constant of the material and thus leading to a frequency independent behaviour. It has been observed that the AC conductivity increases with the frequency of the applied field and the increase in ac conductivity at low frequency is caused by the interfacial polarization whereas at the higher frequency, it is attributed to the electronic polarization.

## Chapter 4. Photo-physical, Electrical, Thermal and Structural investigations of MEH-PPV/PMMA films

This chapter enlists the optical, electrical, thermal and structural investigations of MEH-PPV doped PMMA free standing films. The solution cast film of pure MEH-PPV has absorption in the visible region due to the existence of π-delocalization along the polymer chain**.** For MEH-PPV/PMMA samples, a broad band absorption spectrum with a weak peak at 330nm followed by a strong absorption at 505.3nm has been noticed. The strong absorption peak at 505.3nm corresponds to the excitation from π- π* frontier states and the absorption at 330 nm is the result of forbidden transitions in poly-phenylene derivatives**.** The absorption maxima in the doped films are blue shifted relative to that of pure MEH-PPV film ($\lambda_{max}$= 505.3nm). The increased doping concentration slightly red shifts the maximum absorption wavelength but still it is well below that for pure MEH-PPV film**.** We have noticed that the pristine MEH-PPV film has emission maximum at 588.4nm with a weak shoulder at 630.4nm, assigned to 0–0 & 0–1 electronic transitions. PL spectra are obtained for two different exciting wavelengths 340nmand 450nm revealed that the emission property of MEH-PPV is considerably affected in the presence of PMMA matrix. The emission peaks by the doped samples

are blue shifted relative to pure MEH-PPV for both exciting wavelengths. The maximum blue shift of 85.1 and 69.1nm are noticed for the 0.01% doped sample with the exciting wavelengths 340 and 450nm respectively. With the increase in doping concentration, the emission peak is shifted towards the emission by pure MEH-PPV film causing the reduction in the blue shift. The Stoke's shift (shift relative to the exciting wavelengths) for the samples ranges from 163.3nm for 0.01% doped sample to 194.9 nm for 2% doped sample for the exciting wavelength 340nm and similarly it varies from 69.0 to 85.5nm when excited by 450 nm.

The Urbach energy for pure PMMA sample is 165meV and it is increased to 818meV for MEH-PPV doped PMMA samples. This increase in the Urbach energy is attributed to the increase in the amorphous nature of the doped samples. This result can be correlated with the XRD pattern in which the broad peak intensity corresponding to $2\theta = 14.84$ and $2\theta = 29.1^{\circ}$ is drastically reduced for 0.01% doped sample indicating the increased amorphous nature or reduced crystallinity relative to pure PMMA. With further increase in the doping concentration, the crystallinity is slightly increased but still falls below that of the pure sample. The melting point for the doped films range from 287°C to 299°C and the decomposition temperature is increased from 314°C for PMMA to 369°Cfor 2% doped film, affirming the effect of MEH-PPV on the stability. The phenylene units in MEH-PPV are connected to one another through carbon-carbon double bonds resulting in a rigid structure such that its addition to host will naturally increase the melting point, decomposition temperature and hence the stability. The increase in activation energy with doping level of MEH-PPV confirms the increased thermal stability of the samples as evident from TGA and DTG analysis. FTIR and XRD investigations are reported.

## Chapter 5. Optical, Electrical and Thermal properties of TCNQ doped PMMA Films

The structural, optical, electrical and thermal properties of TCNQ doped PMMA at very low doping concentrations are investigated. PMMA contains an ester functional group, which is polar in nature, and it has dipole interaction as well as Vanderwal's dispersion forces.

Dopant TCNQ being nonpolar in nature, there is no chance of string force of interaction between the host and dopant but due to the polar nature of the host it is possible for the weak dipole induced dipole interaction with the dopant polymer.

The expected characteristic vibration corresponding to cyano group (CN) around 2256cm$^{-1}$ is observed at 2335cm$^{-1}$ affirming its cyano group dragging the lone pair of electrons from the oxygen from the ester group of PMMA, due to which the conjugacy is increased in the resulting blend. The electron density on the cyano (CN) group is increased resulting in the increased frequency of vibration. X ray diffraction studies depicted the reduction in crystallinity of the PMMA. Crystallinity of pure PMMA is 59.89% however for the doped samples it is reduced to 50.36% for 0.007% doped films to 39.65% for 4% TCNQ doped PMMA films. The optical investigations indicate the phase transition of insulating PMMA to the conducting phase as there is rapid decrease in the band gap of the Composite film. There is about 50% decrease in the energy gap of PMMA for the doping concentration from 0.5 to 4wt%. Urbach Energy calculations confirm the electronic transitions among the localized states. The new material exhibits fluorescence in the range 468nm to 496nm when excited by 400nm. A large stokes shift around 98nm has been observed with respect to the wavelength of excitation as well as absorption maximum. The insertion of TCNQ has changed the decomposition nature of PMMA showing enough deviation of TGA curves from that of the undoped PMMA but the maximum decomposition temperature is shifted towards higher temperature region for the doping concentration in the range 0.25% to 4.0% indicating the increased stability. Electrical conductivity and dielectric constants are more for doped sample. The films are transparent and have good dielectric properties so that they can be used in the construction of transparent electrodes and as dielectric films. The films can be used in the construction of optoelectronic devices.

## Chapter 6. Optical, Structural and Morphological Study of Photoactive Blends of modified fullerene with conjugate polymers

We have investigated the UV-VISIBLE absorption spectra for 3:1, 1:1, 1:3 blends of P3HT: PCBM mixed P-N junction photoactive material along with their pristine glass coated films. Spectral analysis indicated that increased weight percentage of PCBM in the blend broadened the spectral region of absorption. The 1:3 blend of P3HT:PCBM showed broad spectral absorption and was selected as the best photoactive blend. The optimized blend had the smallest band gap (1.89eV). In case of MEH-PPV: PCBM blends, also among 3:1, 1:1, 1:3 blends of

photoactive material along 1:3 blend of MEH– PPV with PCBM shows a broad spectral absorption extending from UV region to the region beyond the visible range. Calculation from Tauc's plot gives the band gap of this blend to be 2.05eV. We conclude that 1:3 blend of MEH-PPV:PCBM can be used as the best photoactive material for constructing a plastic solar cell. Similar result is noticed among 3:1, 1:1, 1:3 blends of MDMO-PPV: PCBM blends in which 1:3 blend of MDMO -PPV: PCBM shows a broad spectral absorption. The optical band gap of 1:3 blend is determined to be 1.96eV. By doping with dye or metal nano particles like gold or silver, absorption can be enhanced to harvest maximum solar energy. The SEM images confirmed the formation of multi-P-N junctions in the blend and almost uniform distribution of the PCBM domains in the polymer matrix. Small grain sizes of the dispersed phase justifies the use of Chloro-benzene as the proper solvent. AFM studies confirm the smoothness of the surface accounting for intensive inter chain effects leading to good transport property. Diffused spectra of X-ray diffraction study confirms the dominance of amorphous structure in the blend and suggests the need for improvement in the crystallinity. Thermal annealing can be carried out on the blend during device fabrication for improved device performance. Finally we conclude that 1:3 blends of MDMO-PPV: PCBM, P3HT:PCBM and MEH-PPV:PCBM can be used as the photoactive material for constructing a plastic solar cell and the construction of the solar cell is under progress.

## **Chapter 7.** Summary and Scope for future work

It is the gist of the entire investigations, highlighting the results and their significance. Role of our research work, practical applications and hence its contributions to the field of plastic electronics is discussed. It also covers the scope of future work. The outcome of this research is published in peer reviewed journals, refereed conference proceedings and also as chapters in books of international recognition. The publications and presentations during the tenure of research work are enlisted at the end.

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# List of publications

## i) Journals

1. Switching the photo physics of MDMO-PPV under PMMA environment - a boon for organic electronics. **Ishwar Naik,** R. F. Bhajantri, Vinayak Bhat, B. S. Patil, Vasant S. Naik. *Journal of Polymer Research* 30:133(2023).
2. Achieving the blue phase photo-physics of MEH-PPV through PMMA matrix-A cost effective technique. **Ishwar Naik,** R. F. Bhajantri, Vinayak Bhat, Vasant S. Naik, Ullas N. Shetti, Basavaraj Nimbure, *Chemistry Africa*, CHAF-

D-24-00037(2023).

3. Optically tuned poly (3hexylthiophene2,5diyl)P3HT/PCBM (modified fullerene) blend for plastic solar cells. **Ishwar Naik,** Rajashekhar Bhajantri, Lohit Naik, B. S. Patil, Ullas Shetti, Pragasam, Sunil Rathod, Jagadeesh Naik, *Nanosystems: Physics, Chemistry, Mathematics***,** 2016, 7 (4), p. 691–694(2016).
4. Fullerene Modulated MEH-PPV Photoactive Material for Plastic Solar cells. **Ishwar Naik** , Rajashekhar Bhajantri, B S Patil, Vinayak Bhat. *Materials Science Forum*, Vol. 969, pp439-443.
5. Proton conducting diazanium hydrogen phosphate/poly (vinyl alcohol) electrolytes: Transport, electrical, thermal, structural, and optical properties. Jagadish Naik, RF Bhajantri, Sunil G Rathod, **Ishwar Naik**. *Journal of Elastomers & Plastics* 51(5) 390-405, 2019.
6. Doping-induced modulation of optical properties of PFO/PMMA composite films. Vinayak S. Bhat, S. B. Kapatkar, N. H. Ayachit, **Ishwar Naik** & M. S. Murari *Polym. Bull.* (2020).
7. Microstructural, thermal, and electrical properties of PFO/PMMA composite films Vinayak S Bhat, S.B Kapatkar, **Ishwar Naik** and Shreedatta Hegde *Bull. Mater. Sci.* 45:245(2022).

## ii) Conference Proceedings

1. The Band Gap Tuned, LEP Doped Polymer Films for Plastic Electronics. **Ishwar Naik**, Rajashekhar Bhajantri, Rekha Tandel *AIP Conference Proceedings* 2057, 020031 (2019).
2. Optical and electrical Properties of TCNQ doped PMMA Films. **Ishwar Naik**, Rajashekhar Bhajantri, Pragasam A, Sanjay Suryabhat. *AIP Conference Proceedings* 2104, 030039 (2019).
3. Novel properties of PMMA/PVAc Matrix, Slightly Doped with MDMO-PPV. **Ishwar Naik,** Rajashekhar Bhajantri, Vinayak Bhat. *AIP Conference Proceedings* 2104, 030040 (2019).
4. Spectrally Tuned P3HT/TCNQ Bulk P-N Junction Blend for Plastic Solar Cell **Ishwar Naik**, Rajashekhar Bhajantri. *Materials today: Proceedings 3(10)Part B*, 3608-3613(2016).
5. Drastic Reduction in the Band Gap-A Novel Material for Plastic Electronics. **Ishwar Naik,** Rajashekhar Bhajantri. *Materials today: Proceedings 5(10) Part 1*, Pages 21523-21528(2018).
6. Nano tuned conducting polymer for plastic solar cell . **Ishwar Naik**, Rajashekhar Bhajantri, Vinayak Bhat, B.S Patil. *IOP Conf. Series: Materials Science and Engineering 3*96-012048(2018)**.**
7. Plasmon Resonance In Photoactive P-N Junction Blend, Spin Coated From Self-made Low Cost Spin Coating Machine For Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri, Sunil Rathod, Jagadish Naik. *Advanced Materials Proceedings*, Volume 2, pp 325-328;

8. Perylene Tuned Spectral Response of MDMO-PPV for Plastic Solar Cell. **Ishwar Naik,** Rajashekhar Bhajantri. *Advanced Science letters* 23(3):1892-1894(2017).
9. Dielectric, thermal and mechanical properties of ADP doped PVA composites. Jagadish Naik, R. F. Bhajantri, V. Ravindrachary, Sunil G. Rathod, T. Sheela, and **Ishwar Naik.** *AIP Conference Proceedings,*1665, 040005 (2015).

## iii) Book Chapters

1. Spectral Tuning of P3HT/PTCDA Bulk HeteroP-N Junction Blend for Plastic Solar Cell . **Ishwar Naik**, Rajashekhar Bhajantri and Jagadish Naik *Applied Physical Chemistry with Multidisciplinary Approaches,* Apple Academic Press, (USA) and CRC Press, Taylor and Francis group, Hard ISBN**:** 9781771886062 E-Book ISBN: 9781315169415 Pub Date: May 2018.
2. Optically Tuned MDMO-PPV/PCBM Blend for Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri, and Jagadish Naik, *Nanotechnology-Driven Engineered Materials New Insights,* Apple Academic Press, (USA) and CRC Press Taylor and Francis group Hard ISBN**:** 9781771886345 E-Book ISBN**:** 978-1-77188-634-5,Pub Date**:** August 2018

# Presentations in Conference/Symposia

1. Tuning the Band Gap of Light Emitting Polymer MDMO-PPV for Plastic Electronics. **Ishwar Naik,** Rajashekhar Bhajantri. International Conference On Direct Digital Manufacturing & Polymers, **ICDDMAP-2015** at Karnatak University, Dharwad, 28$^{th}$ -31$^{st}$ Oct 2015.
2. Dye Sensitization of Optically Tuned MDMO-PPV/PCBM (Modified Fullerene) Bulk P-N Junction Blend For Plastic Solar Cells. **Ishwar Naik**, Rajashekhar Bhajantri, International Conference on Nano Structured Polymeric Materials & Polymer Nanocomposites, **ICNPM-2015** at Mahatma Gandhi, University, Kottayam, Kerala. 13-15 Nov 2015.
3. Optically Tuned P3HT/PCBM Blend for Plastic Solar Cell. **Ishwar naik**, Rajashekhar Bhajantri. International Conference On Nano Materials & Nano Technology**, NANO-15** at KSR College Of Technology, Tamilnadu, 7-10$^{th}$ Dec 2015.
4. Spectral Tuning Of P3HT-PTCDA Bulk Hetero P- N Junction Blend For Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri, International Conference On Advanced Materials For Power Engineering, **ICAMPE-2015** at Mahatma Gandhi University, Kottayam, Kerala,11$^{th}$-13$^{th}$ Dec 2015.
5. Fullerene (PCBM) Modulated MEH-PPV Photoactive Material For Plastic Solar Cells. **Ishwar Naik**, Rajashekhar Bhajantri. International Conference on Nano Science, Nanotechnology & Advanced Materials, **NANOS-2015** at GITAM University, Visakhapatnam, AP,14$^{th}$ -17$^{th}$ Dec 2015.

6. Perylene Tuned Spectral Response Of MDMO-PPV for Plastic Solar Cells. **Ishwar Naik**, Rajashekhar Bhajantri, International Conference On Healthcare & Technical Research, **ICHTR-2015** at Manipal University, Manipal, Karnataka.22-24$^{th}$ Dec 2015.
7. Dye Doped Soft Matter Pedot-Pss/Pvp Film For Plastic Electronic Devices – Solar Cell & Diode. **Ishwar Naik,** Rajashekhar Bhajantri. National Conference on Modern Materials Devices & Applications at Maharani Science College For Women, Bangalore, Karnataka.7$^{th}$, 8$^{th}$ Jan 2016.
8. Spectrally Tuned P- N Junction Blend For Plastic Solar Cell**. Ishwar Naik**, Rajashekhar Bhajantri, International Conference On Mathematics, Physics & Allied Sciences, **ICMPAS-2016** at Carmel College, Goa, 3$^{rd}$ -5$^{th}$ March 2016.
9. Plasmon Resonance in P-N junction Blends Spin Coated from Self Made Low Cost Spin Coating Machine for Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri, Sunil Rathod, Jagadeesh Naik. International Conference On Material Science & Technology, **IMTECH-2016** at Delhi University, Delhi 1$^{st}$ -4$^{th}$ March 2016.
10. Spectrally Tuned P3HT/TCNQ Bulk P-N Junction Blend for Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri. International Conference On Materials Research & Applications, **ICMRA-2016** at CMR Technical Campus, Hyderabad.11$^{th}$ -13$^{th}$ March 2016.
11. Optimizing MEH-PPV/$TiO_2$ Nanocomposites P-N Junction Photoactive Blend for Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri. DAE-BRNS Symposium on Condensed matter physics under extreme conditions, **CoMPEC-2016** organized by BARC, Mumbai,13$^{th}$ – 16$^{th}$ April 2016.
12. A Novel Band Gap and a Smart Material for plastic Electronics. **Ishwar Naik**, Rajashekhar Bhajantri. Second International Conference on Healthcare and Technical Research **ICHTR -2016** held at Manipal University,7 - 8 December 2016.
13. Nano composite Photoactive P-N junction blend for Plastic Solar cell. **Ishwar Naik** , Rajashekhar Bhajantri. International Conference on 'Recent Innovations in Civil and Mechanical Engineering' **i–CAM 2k16** held at CMR Technical Campus Hyderabad, 10$^{th}$ and 11$^{th}$ December 2016.
14. Drastic Reduction in the Band gap - A Novel Material for Plastic Electronics. **Ishwar Naik** , Rajashekhar Bhajantri. International Conference on Smart Engineering Materials **ICSEM-2016** held at RV College of Engineering, Bengaluru, 20$^{th}$ -22$^{nd}$ October 2016.
15. Fullerene Tuned MEH-PPV, a Bulk Junction Blend for Plastic solar cell. **Ishwar Naik**, Rajashekhar Bhajantri, B S Patil, Vinayak Bhat, International Symposium on Functional Materials **ISFM-2016** Organized by IIT Kanpur, Panjab University and University of Illinois at Chicago, held at Chandigarh 13$^{th}$ -15$^{th}$ April 2018.
16. Optically optimized PN junction Blend for Plastic Solar Cell. **Ishwar Naik** , Rajashekhar Bhajantri, International Conference on Renewable Energy Research and Education, **RERE-2018** Organized by Govt Autonomous College, Rajamahendravaram, Andhrapradesh, 8$^{th}$ -10$^{th}$ Feb 2018.

17. Optically Tuned Light Emitting Polymer for Plastic Electronics. **Ishwar Naik**, Rajashekhar Bhajantri, International Conference on Advances in Material Science **ICAMS-2018** held at Shri Shankara College, Kalady, Kerala 24th and 25th October 2018.
18. Nano Tuned Conducting Polymer for Plastic Solar Cell. **Ishwar Naik**, Rajashekhar Bhajantri, Vinayak Bhat, B.S Patil. Second Global Colloquium on Recent Advancements and Effectual Researches in Engineering , Science and Technology **RAEREST-2018** held at St. Joseph's College of Engineering and Technology Palai, Kerala, 20th and 21st April 2018.
19. Fullerene Modulated MEH-PPV Photoactive Material for Plastic Solar cells. **Ishwar Naik** , Rajashekhar Bhajantri, B S Patil, Vinayak Bhat. International Conference on Recent Advances in Materials and Manufacturing Technogies, **ICRAMMT-2018** held at MLR institute of Technology and Management, Dundigal, Hyderabad on 19th and 20th November 2018.
20. The Band Gap Tuned, LEP Doped Polymer Films for Plastic Electronics. **Ishwar Naik**, Rajashekhar Bhajantri, Rekha Tandel. Second International Conference on Polymer Composites **ICPC-2018** held at NITK Surathkal, 15th and 16th December 2018.
21. Optical and electrical Properties of TCNQ doped PMMA Films.**Ishwar naik**, RajashekharaBhajantri,Pragasam A , Sanjay Suryabhat. International Conference on Multidimensional Role of Basic Science in Advanced Technology **ICMBAT-2018**, held at KDK College ,Nagpur 14-15December 2018.
22. Novel properties of PMMA/PVAc Matrix, Slightly Doped with MDMO-PPV **Ishwar naik**, Rajashekhar Bhajantri, Vinayak Bhat. International Conference on Multidimensional Role of Basic Science in Advanced Technology **ICMBAT-2018(),** held at KDK College ,Nagpur 14-15 December 2018.
23. Solar Cell material Designed from self-made Low cost spin Coating machine **Ishwar Naik** , Rajashekhar Bhajantri, B S Patil. Interdisciplinary Conference on Health Care and Technical Research **ICHTR 2017** Manipal Academy of higher Education Udupi,4-8 December 2017.
24. A smart material for plastic electronic devices. **Ishwar Naik**, Rajashekhar Bhajantri, Sanjay Suryabhat. National conference on Particle Accelerators in Interdisciplinary Research **PAIR-2017** conducted by Mangalore University. 11-13April 2017.

# Projects Completed

1. **UGC Minor Research Project (MRP)** entitled "The Construction and Characterization of an Organic Solar Cell (Organic Photovoltaic Cell-OPV) Devised from Self-made Low Cost Spin Coating Machine" UGC Reference No. F.MRP/12th Plan/14-15/KAKA 088dated 10th December-2014, Amount 4,80,000/-
2. **Student Project SPICE – 2015** entitled Tuning the Band Gap of conducting Polymers for Plastic Electronics VGST/SPiCE 276/2014-15 dated 03-03-2015 amount 30,000/-

# Orientation/Refresher/Workshop/Training Course4es Attended during the Period of Research

1. Participated in the UGC sponsored Refresher Course in Environmental Studies (Interdisciplinary) held from 10th -30th January 2017, at Human Resource Development Centre Goa University.
2. Participated in 7 days Training Course for NSS Programme officers organized by NSS- Empaneled Training Institution for Karnataka, University of Mysore from 20th-26th July 2017.
3. Two Week Faculty Development Program on "Multimedia and Drawing" from 3rd- 16th June 2020 organized by Department of Computer Science, Government First Grade College, Harihara, Karnataka in association with Spoken Tutorial IIT Bombay (An Initiative of National Mission of Education through ICT, MHRD) under the scheme PMMMNMTT.
4. One Week Faculty Development Program on "Open-Source Tools for Research from 8th to14th June 2020 organized by Teaching Learning Centre, Ramanujan College, University of Delhi sponsored by Ministry of Human Resource Development (MHRD)and PMMMNMTT.
5. One-week Online Short-term Training Program on "Recent Development of Advanced Materials and its Applications in Technology" from17th -22nd June 2020 KDK College of engineering in collaboration with Bhiwapur Mahavidyalaya, Society for Technologically Advanced material of India (STAMI) and Luminescence Society of India (LSI).
6. 64th Online Short term course on "E-Content Development" from 25thJune to 1st July 2020 organized by UGC-Human Resource Development Centre, Gujarat University, Ahmedabad.

# Awards/ Recognitions

1. Best Paper Award for Oral Presentation in National Level Seminar held at C S Bembalagi College, Ramdurg on 11th Sep 2015.
2. Awarded with First Prize for Oral Presentation in International Seminar ICHTR-2015 held at Manipal University, Manipal on 22nd-24th Dec 2015.
3. Awarded with First Prize for Oral Presentation in National Seminar held at Maharani Science College, Bangalore on 7th-8th Jan 2016.
4. Chaired session at international conference ICNPM at Mahatma Gandhi University Kerala Kottayam on 13th-15th Nov 2015.
5. Chaired session at international conference ICAMPE at Mahatma Gandhi University Kottayam Kerala on11th -13th Dec 2015.
6. Worked as the convener for the International Conference on Going Global in

Higher Education (GGHE-2K19) held in Govt Arts and Science College, Karwar, on Feb 28th and March 1st of 2019.

7. Worked as convener for two days Indo-US online International conference in collaboration with Tandon School of America in 2020.
8. Worked as the convener for International Conference on Growing Research Aspirations at Collegiate Education (GRACE-2023) held at GFGC Kumta, on 11-12 December 2023.

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| Dr. R. F.Bhajantri<br>Research Supervisor<br>Scholar<br>Date: | Naik Ishwar K<br>Research<br><br>Date: |

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